

USE OF SULFONATED POLYSTYRENE POLYMERS  
IN HARD SURFACE CLEANERS TO PROVIDE  
EASIER CLEANING BENEFIT

Field of the Invention

This invention relates to the use of sulfonated polystyrene polymers in hard surface cleaners.

Background of the Invention

Hard surface cleaners typically contain nonionic surfactants, an anti-bacterial agent (which may be a quaternary ammonium type surfactant), chelating agents, a solvent, and water. Optionally, anionic surfactants may be used in which case the anti-bacterial agent may be excluded or replaced by something other than a quaternary ammonium-type surfactant. The most common surfactant systems for household cleaners are alkyl polyglucosides, or alkyl ethoxylates.

Hard surface cleaners are formulated so as to provide cleaning benefit, with little or no foam, and very fast drying so as to leave little or no streaking or residue. The surfactants and solvents provide most of the cleaning benefits, and the surfactants may leave some residual hydrophilization benefit to the surface. Hydrophilization can improve the ease of cleaning, by tending to repel any hydrophobic soils from adhering strongly to a surface. However, the ease of cleaning benefit if present is short lived, since upon any rinsing or wiping the surfactant may be easily rinsed away. This is particularly true in the case of hydrophobic surfaces.

Hydrophilic surfaces inherently repel hydrophobic soils to some degree. Less polar or non-polar surfaces, however, do not naturally possess attributes for repelling soils which are typically hydrophobic in nature.

#### Summary of the Invention

In one aspect, the present invention is directed to an aqueous hard surface cleaner composition comprising:

a surfactant selected from the group consisting of nonionic surfactants, cationic surfactants, amphoteric surfactants, zwitterionic surfactants and mixtures thereof,

a germicidal agent, which may be absent if the surfactant comprises a quaternary ammonium surfactant,

a hydrophilic polymer comprising styrene sulfonate repeating units, and

water,

wherein the composition exhibits a pH of greater than or equal to about 6.

In another aspect, the present invention is directed to a method for cleaning a hard surface, comprising contacting the hard surface with the above described aqueous hard surface cleaner.

The composition of the present invention provides an easier cleaning benefit, wherein easier cleaning is identified by comparing the ease of removing a soil from a surface which had, prior to soiling, been cleaned with the hard surface cleaner composition of the present invention to the ease of removing a soil from the surface which had, prior to soiling, been cleaned with the hard surface cleaner that lacks the hydrophilic polymer component

of, but is otherwise analogous to the hard surface cleaner composition of the present invention.

#### Detailed Description of Invention and Preferred Embodiments

Suitable hard surfaces are smooth, substantially non porous surfaces including, for example, glass, ceramic, organic polymer, metal, or wood.

In one embodiment, the hard surface cleaner composition of the present invention comprises, based on 100 parts by weight (pbw) of such composition,

from about 0.01 to about 10 pbw, more typically from about 0.01 to about 5 pbw, of the surfactant,

a germicidally effective amount of the germicidal agent,

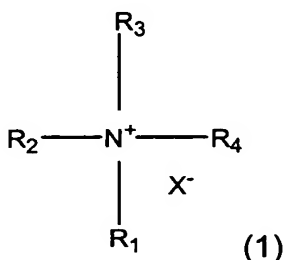
from about 0.01 to about 10 pbw, more typically from about 0.01 to about 3 pbw, of the hydrophilic polymer, and

and water

Nonionic surfactants are surfactant compounds that do not dissociate into ions and that do not have an electrical charge associated with them. Suitable nonionic surfactants are generally known in the art and include, for example, compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature. Examples of useful nonionic surfactants include the polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols, fatty acid amide surfactants, polyhydroxy fatty acid amide surfactants, amine oxide surfactants, alkyl ethoxylate surfactants, alkanoyl glucose amide surfactants, alkanolamides surfactants, alkylpolyglycosides, and condensation products of aliphatic alcohols with

from about 1 to about 25 moles of ethylene oxide. Specific examples of suitable nonionic surfactants include alkanolamides such as cocamide DEA, cocamide MEA, cocamide MIPA, PEG-5 cocamide MEA, lauramide DEA, and lauramide MEA; alkyl amine oxides such as lauramine oxide, cocamine oxide, cocamidopropylamine oxide, and lauramidopropylamine oxide; polysorbates and ethoxylated sorbitan esters such as sorbitan laurate, sorbitan distearate, PEG-80 sorbitan laurate, polysorbate-20, and polysorbate-80; fatty acids or fatty acid esters such as lauric acid, isostearic acid, and PEG-150 distearate; fatty alcohols or ethoxylated fatty alcohols such as lauryl alcohol, laureth-4, laureth-7, laureth-9, laureth-40, trideceth alcohol, C11-15 pareth-9, C12-13 Pareth-3, and C14-15 Pareth-11, as well as mixtures thereof.

Cationic surfactants are ionic surfactant compounds that have a positive electrical charge associated with the hydrophilic portion of the surfactant. Suitable cationic surfactants are generally known in the art and include, for example, compounds according to formula (1) below:



wherein:

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>, are each independently hydrogen, an organic group, provided that at least one of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> is not hydrogen.

X<sup>-</sup> is an anion.

Suitable anions include, for example, chloride, bromide, methosulfate, ethosulfate, lactate, saccharinate, acetate or phosphate.

If one to three of the  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  groups are hydrogen, then the compound may be referred to as an amine salt. Some examples of cationic amine salts include polyethoxylated (2) oleyl/stearyl amine, ethoxylated tallow amine, cocoalkylamine, oleylamine, and tallow alkyl amine as well as mixtures thereof.

For quaternary ammonium compounds (generally referred to as "quats")  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  may each independently be the same or different organic group, or alternatively, may be fused with another one of the  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  groups to form, together with the nitrogen atom to which they are attached, a heterocyclic ring, but may not be hydrogen. Suitable organic groups include, for example, alkyl, alkoxy, hydroxyalkyl, and aryl, each of which may be further substituted with other organic groups. Suitable quaternary ammonium compounds include monoalkyl amine derivatives, dialkyl amine derivatives, and imidazoline derivatives, as well as mixtures thereof.

Suitable monoalkyl amine derivatives include, for example, cetyl trimethyl ammonium bromide (also known as cetrimonium bromide or CETAB), cetyl trimethyl ammonium chloride (also known as cetrimonium chloride), myristyl trimethyl ammonium bromide (also known as myrtrimonium bromide or Quaternium-13), stearyl dimethyl benzyl ammonium chloride (also known as stearalkonium chloride), oleyl dimethyl benzyl ammonium chloride, (also known as olealkonium chloride), lauryl/myristyl trimethyl ammonium methosulfate (also known as cocotrimonium methosulfate), cetyl-dimethyl-(2)hydroxyethyl ammonium

dihydrogen phosphate (also known as hydroxyethyl cetyldimonium phosphate), bassuamidopropylkonium chloride, cocotrimonium chloride, distearyldimonium chloride, wheat germ-amidopropalkonium chloride, stearyl octyldimonium methosulfate, isostearaminopropal-konium chloride, dihydroxypropyl PEG-5 linoleaminium chloride, PEG-2 stearamonium chloride, Quaternium 18, Quaternium 80, Quaternium 82, Quaternium 84, behentrimonium chloride, dicetyl dimonium chloride, behentrimonium methosulfate, tallow trimonium chloride, and behenamidopropyl ethyl dimonium ethosulfate, as well as mixtures thereof.

Suitable dialkyl amine derivatives include, for example, distearyldimonium chloride, dicetyl dimonium chloride, stearyl octyldimonium methosulfate, dihydrogenated palmoylethyl hydroxyethylmonium methosulfate, dipalmitoylethyl hydroxyethylmonium methosulfate, dioleoylethyl hydroxyethylmonium methosulfate, hydroxypropyl bisstearyldimonium chloride, and mixtures thereof.

Suitable imidazoline derivatives include, for example, isostearyl benzylimidonium chloride, cocoyl benzyl hydroxyethyl imidazolinium chloride, cocoyl hydroxyethylimidazolinium PG-chloride phosphate, Quaternium 32, and stearyl hydroxyethylimidonium chloride, and mixtures thereof.

Amphoteric surfactants are ionic surfactant compounds that are characterized by the presence of two ionic sites on the same molecule and which, depending on the pH of the surrounding medium, may carry a negative electrical charge, a positive electrical charge, or both a negative electrical charge and a positive electrical charge on the same molecule. Suitable amphoteric surfactants are generally known in the art and include, for example, derivatives of aliphatic secondary and tertiary amines in which

the aliphatic radical may be straight chain or branched, may be saturated or unsaturated, and wherein one of the aliphatic substituents contains from about 8 to about 22 carbon atoms and one contains an anionic water solubilizing group. Specific examples of suitable amphoteric surfactants include the alkali metal, alkaline earth metal, ammonium or substituted ammonium salts of alkyl amphocarboxy glycines and alkyl amphocarboxypropionates, alkyl amphodipropionates, alkyl amphodiacetates, alkyl amphoglycines and alkyl amphopropionates, as well as alkyl iminopropionates, alkyl iminodipropionates and alkyl amphopropylsulfonates. Amphoteric surfactants are typically associated with a counterion, such as, for example, a sodium, magnesium, potassium, ammonium, or substituted ammonium cation. Specific examples of some suitable amphoteric surfactants include sodium cocoamphoacetate, sodium cocoamphopropionate, disodium cocoamphodiacetate, diammonium cocoamphodiacetate, sodium lauroamphoacetate, disodium lauroamphodiacetate, dipotassium lauroamphodiacetate, dimagnesium lauroamphodiacetate, disodium lauroamphodipropionate, disodium cocoamphopropyl sulfonate caproamphodiacetate, sodium caproamphoacetate, disodium caproamphodipropionate, and sodium stearamphoacetate, and triethanolamine stearamphoacetate, as well as mixtures thereof.

Zwitterionic surfactants are ionic surfactant compounds characterized by the presence of two ionic sites per molecule, wherein one of the ionic sites carries a positive electrical charge regardless of the pH of the surrounding medium and wherein the other ionic site may, depending on the pH of the surrounding medium, carry a positive charge. Suitable zwitterionic surfactants are generally known in the art and include, for example, those which can be broadly described as derivatives of aliphatic

quaternary ammonium, phosphonium, and sulfonium compounds in which the aliphatic radicals may be straight chain or branched, may be saturated or unsaturated, and wherein one of the aliphatic substituents contains from about 8 to 22 carbon atoms and one contains an anionic water-solubilizing group such as carboxyl, sulfonate, sulfate, phosphate or phosphonate. Specific examples of suitable Zwitterionic surfactants include alkyl betaines, such as cocodimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alpha-carboxy-ethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxy-ethyl)carboxy methyl betaine, stearyl bis-(2-hydroxy-propyl)carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine, amidopropyl betaines, and alkyl sultaines, such as cocodimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxy-ethyl)sulfopropyl betaine, and alkylamidopropylhydroxy sultaines, as well as mixtures thereof.

The germicidal component of the hard surface cleaner of the present invention may be any compound which exhibits germicidal activity, that is, is capable of killing bacteria and/or retarding bacterial growth, on a hard surface to which the hard surface cleaner of the present invention is applied, including, for example, sodium hypochlorite and quaternary ammonium compounds.

A germicidally effective amount of a quaternary ammonium compound is typically from about 0.01 to about 10 pbw, more typically from about 0.01 to about 3 pbw quaternary ammonium compound per 100 pbw of the hard surface cleaner composition of the present invention.



Quaternary ammonium compounds suitable for use as the germicidal agent of the hard surface cleaner of the present invention include the quaternary ammonium surfactants described above. If the surfactant component of the composition of the present invention comprises at least a germicidally effective amount of a quaternary ammonium surfactant, then such quaternary ammonium surfactant may also function as the germicidal agent, in which case no separate germicidal agent is required.

In one embodiment, the primary surfactant is selected from semi-polar nonionic surfactants, alkylbetaine or sulfobetaine amphoteric surfactants, and mixtures thereof.

The hard surface cleaner composition of the present invention may, optionally, further comprise a water soluble organic solvent. Suitable water soluble organic solvents are generally known in the art and include, for example, (C<sub>1</sub>-C<sub>6</sub>)alkanols, (C<sub>1</sub>-C<sub>6</sub>)diols, (C<sub>3</sub>-C<sub>24</sub>)alkylene glycol ethers, and mixtures thereof. In one embodiment, the composition of the present invention further comprises up to about 10 pbw of a water soluble organic solvent per 100 pbw of the hard surface cleaner composition of the present invention.

The hard surface cleaner composition of the present invention may, optionally, further comprise a chelating agent. Suitable chelating agents for chelating metal atoms are generally known in the art and include, for example, aminophosphonate chelating agents, and ethylenediamine tetraacetic acid. Suitable aminophosphonate chelating agents include, for example, ethylene diaminetetramethylene phosphonates, diethylene triamine pentamethylene phosphonate. In one embodiment, the chelating agent comprises ethylenediamine tetraacetic acid. In one embodiment, the composition of the

present invention further comprises, based on 100 pbw of the hard surface cleaner composition of the present invention, from about 0.01 to about 10 pbw, more typically from about 0.1 to about 3 pbw, of a chelating agent.

The hydrophilic polymer of the present invention may be any polymer that contains styrenesulfonate repeating units, including styrenesulfonate homopolymers, such as poly(sodium 4-styrenesulfonate) polymers, as well as copolymers that contain styrenesulfonate repeating units copolymerized with repeating units derived from one or more other monoethylenically unsaturated monomers. Suitable ethylenically unsaturated monomers include, for example, styrene, acrylic acid, methacrylic acid, crotonic acid, itaconic acid, vinyl acetic acid, maleic acid, fumaric acid, (C<sub>1</sub>-C<sub>4</sub>)alkyl esters of acrylic acid or methacrylic acid, such as methyl acrylate and methyl methacrylate, (C<sub>1</sub>-C<sub>4</sub>)hydroxyalkyl esters of acrylic acid or methacrylic acid, such as hydroxyethyl methacrylate. Suitable copolymers include random copolymers, graft copolymers and block copolymers, such as, for example, poly(styrenesulfonic acid co-maleic acid) sodium salt, poly(sodium 4-styrenesulfonate) -poly(styrene) random copolymers, poly(sodium 4-styrenesulfonate) -b- poly(acrylamide) block copolymers, poly(sodium 4-styrenesulfonate) -b- poly(styrene) block copolymers, poly(sodium 4-styrenesulfonate) -b- poly(hydroxyethylmethacrylate) block copolymers, and poly(sodium 4-styrenesulfonate) -b- poly(methacrylic acid) block copolymers.

In one embodiment, a suitable copolymer comprises, on average,, greater than or equal to about 1 mole styrene sulfonate repeating units per 100 moles of repeating units of the copolymer. In those embodiments wherein the comonomer of such copolymer is a hydrophobic comonomer, such as for example, styrene, such copolymers more typically comprise, on average, greater than or equal to about 20 moles, even more typically 40

moles, styrene sulfonate repeating unit per 100 moles of repeating units of the copolymer.

In one embodiment, the hydrophilic polymer exhibits a weight average molecular weight (MW) of greater than or equal to about 1000, more typically of from about 5,000 to about 5,000,000, and even more typically of from about 10,000 to about 2,000,000, as determined by gel permeation chromatography (GPC).

In one embodiment, the hard surface cleaner composition of the present invention exhibits a pH of from about 7 to about 14, more typically a pH of from about 7 to about 13, and even more typically a pH of from about 8 to about 13.

The hard surface cleaner composition of the present invention may, optionally, further comprise up to about 10 pbw per 100 pbw of the hard surface cleaner composition of other ingredients, such as for example, fragrances, colorants, opacifiers, bleaching agents, pH modifiers, detergent enzymes, stabilizers, germicidally active components, thickeners, hydrotropes.

The hard surface cleaner composition of the present invention is made by combining and mixing desired appropriate relative amounts of the above described components.

In one embodiment of the method of the present invention, a hard surface is contacted with the hard surface cleaner of the present invention and the hard surface cleaner composition and the surface is rinsed with water or wiped and allowed to dry.

Use of the hard surface cleaner to clean a hard surface renders the surface easier to clean in subsequent cleaning activities. While not wishing to be bound by theory, it is believed that some of the hydrophilic polymer component of the cleaner composition remains on the surface after cleaning and disrupts interaction between the surface and hydrophobic soil that subsequently comes into contact with the surface, thus rendering the soil easier to remove from the surface.

#### Examples 1-10 and Comparative Examples C1 and C2

The easier cleaning benefit provided by treatment of a hard surface with a polymer comprising styrenesulfonate repeating units was measured by treating the surface of Formica laminate tiles with such polymers, soiling the surfaces, and then scrubbing the surfaces and rating the level of cleanliness of the scrubbed surfaces.

A scrub tester apparatus was used. The scrub tester consisted of a wooden panel ( about 40cm in length) with rails to hold 8 samples tile in a single row, and a metal track with rails for guiding a sponge holder placed over the panel in order to wipe tiles.

Formula 409 (Antibacterial Formulation) All Purpose Cleaner was used as comparative Example C1 and Fantastik All Purpose Cleaner was used as comparative Examples C2. The Formula 409 cleaner exhibited a pH of about 12.3. The Fantastik cleaner exhibited a pH of about 12.2.

The cleaner compositions of Examples 1-10 each included 1 wt% hydrophilic polymer and were made by adding the hydrophilic polymer listed

in TABLE I below to Formula 409 (Antibacterial Formulation) All Purpose Cleaner (Clorox). The pH of each of the compositions of Examples 1-10 was adjusted to a value of  $12.3 \pm 0.1$ .

Substrate tiles (5cm x 5cm white Formica<sup>TM</sup> laminate squares mounted on 1.3cm thick particle board) were pre-cleaned by the addition of 0.1 mL of ethanol onto the surface of the tile and wiped with paper towel. The tiles are allowed to dry at room temperature for at least 30 min.

The substrate tiles were treated as follows. 1.0 mL of a treatment formulations listed in the TABLE below was pipetted onto the surface of a pre-cleaned tile. The formulation was spread over the entire upper surface of the tile and allowed to remain on the surface of the tile for five minutes. The upper surfaces of the tiles were then wiped three times with each side of a water dampened 4cm x 4cm cellulosic sponge and allowed to dry at room temperature for 2-3 hours.

A test soil was made by combining 20.0 g of a curing agent and 90 g of a soil stock and mixing the combination for 4-5 hours. The soil stock was made by mixing 60 g sunflower oil, 10 g olive oil, and 20 g iron oxide pigment in a 150 ml plastic beaker with stir bar at room temperature for approximately 30 min. A curing agent was made by mixing 45 g isooctane and 1 g cobalt naphthenate in a 150 ml plastic beaker with stir bar at room temperature for approximately 30 min.

Lightly soiled substrate tiles were prepared as follows. Eight tiles were mounted in the scrub tester. A 4 inch wide soft rubber ink roller was dampened with the test soil. Single drops of test soil were applied to the third and fifth tiles and the drops were then spread evenly over the four inner

tiles using the dampened roller. The tiles were placed in a constant temperature and humidity chamber (25°C, 50 % RH) for 24 h.

Heavily soiled substrate tiles were prepared as follows. Eight tiles were mounted in the scrub tester. Single drops of test soil were deposited on the third and fifth tiles and the drops were spread over the four inner tiles using a soil dampened 4 inch wide soft rubber ink roller. Single drops of test soil were then deposited on the second and fourth tiles and the drops were spread over the four inner tiles using the soil dampened roller. The tiles were then placed in a constant temperature and humidity chamber (25°C, 50 % RH) for 24 h.

The soiled substrate tiles were scrubbed. Eight tiles were mounted in the scrub tested. In each case, the four inner tiles were the test specimens of interest and the outer tile were simply place holders. A 4cm x 9cm cellulosic sponge was rinsed in water and rung out by hand, so that it was damp but is not dripping wet. The sponge was placed into the metal sponge holder. The cleaner was sprayed a few times so there is a consistent strong spray for the test. The first two soiled tiles were sprayed once (about 1.3 g) with cleaner from about 4 inches away. Immediately spray the second two soiled tiles were then sprayed once with cleaner from about four inches away.. The sponge in its metal holder was placed on the track and moved from one end of the track to the other for 10 counts (wherein one count is from one end of the track to the other) to scrub the tiles in the scrub tester. The inner tiles were removed from the scrub tester, examined and rated on a scale of 0 to 5 (0-is no removal and 5 is total removal) for soil removal. Results are given in TABLE I below. Each rating is based on the average for 8 cleaned tiles.

TABLE I

Ex. #	Styrene Sulfonate Polymer	Molar ratio (Styrene sulfonate units:comono mer units)	Light soil	Heavy soil
C1	None	--	1	0.5
C2	None	--	1	0.5
1	Poly(sodium 4-styrenesulfonate), MW =1,000,000	--	4.3	2.8
2	Poly(sodium 4-styrenesulfonate), MW =200,000	--	2	0.5
3	Poly(sodium 4-styrenesulfonate), MW =70,000	--	3.25	1
4	Poly(styrenesulfonic acid co-maleic acid) sodium salt MW =20,000	1:1	4	2.8
5	Poly(styrenesulfonic acid co-maleic acid) sodium salt MW =20,000	3:1	4.5	3.8
6	Poly(sodium 4-styrenesulfonate) -b- poly(acrylamide) block copolymer 5,000 ≤ MW ≤ 30,000	5.3:94.6	4	0.5
7	Poly(sodium 4-styrenesulfonate) -b- poly(styrene) block copolymer 500 ≤ MW 1,000	92.2:9.6	2.3	3
8	Poly(sodium 4-styrenesulfonate) -b- poly(hydroxyethylmethacrylate) block copolymer 5,000 ≤ MW ≤ 10,000	75:25	2.5	1
9	Poly(sodium 4-styrenesulfonate) - poly(methacrylic acid) random copolymer MW < 10,000	80:20	3.5	1
10	Poly(sodium 4-styrenesulfonate) -b- poly(styrene) random copolymer MW = 30,000	40:60	4.5	3.5

### Example 11

A hard surface cleaner composition is made by combining the ingredients listed below in TABLE II in the relative amounts set forth in TABLE II.

TABLE II

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<b>Ingredient</b>	<b>Amount (pbw per 100 pbw composition)</b>
Na <sub>4</sub> EDTA	0.5
Tallow Benzyl Quat (Lonza)	0.27
Rhodasurf LA-7	2.25
poly(sodium 4-styrenesulfonate) MW = 1,000,000	1
Water	Balance to 100 pbw